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EXAFS and XANES study of (Si, Ge) mullite gels and glasses prepared by slow hydrolysis of alkoxides

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Local structures in optically clear gels, glasses and mullite ceramics in the Al_2O_3–SiO_2–GeO_2 system have been studied using X-ray absorption spectroscopy at the aluminium, silicon and germanium edges. In mullite, $3Al_2O_3$–$2SiO_2$, and the corresponding germanates, both in gel and thermally treated phases, as well as in $8Al_2O_3$–$2SiO_2$ and Al_2GeO_5, aluminium is in a hexacoordinate environment, the extent of distortion of which is variable. For the last-mentioned aluminogermanate, GeO_4 tetrahedra are rapidly formed, and the local environment within the first shell remains stable up to the ceramic state. Longer distance order is observed for the gel and crystal phases, but not for the intermediate glasses. Si–O bonds are longer in mullite gels than the corresponding ceramics, probably due to the existence of bridging hydroxyl groups in the former.

1. Introduction

Sol–gel methods, in particular the hydrolysis of alkoxides, are reputed to lead to products that are homogeneous on the molecular scale [1]. In the Al_2O_3–SiO_2–GeO_2 system, the gels obtained are amorphous and undergo transformation into porous glasses which densify on crystallisation [2]. Earlier work has shown that this process is directly related to the presence of hydroxide ions which cover the porous surface and stabilise the polymeric structure of the oxide [3]. The structure of gels and glasses in this system is, however, less well understood. Results from NMR, Raman and infrared spectroscopies have provided a basis on which descriptions for some compositions have been made [4–6]. Better adapted to the study of short-range ordering in such materials, X-ray absorption spectroscopy has now been applied to study the evolution of local structure of aluminosilicates (germanates) of the mullite type, from the gel state up to the orthorhombic phase, by EXAFS and XANES analyses at the aluminium, silicon and germanium absorption edges of various phases in the Al_2O_3–SiO_2–GeO_2 system. Only limited use has been made up to now of this approach [7].

2. Experimental

2.1. Synthesis

Gel samples were prepared by slow hydrolysis of mixtures of aluminium butoxide and either silicon methoxide or germanium ethoxide in hexane, following methods described previously [5,8] for the synthesis of aluminosilicates and aluminogermanates respectively. Monolithic gels, which remain optically clear up to ~1400°C (aluminosilicates) and ~1100°C (aluminogermanates) are obtained after 6–8 months and 12–

15 months, respectively. Rapid hydrolysis of a solution of aluminium butoxide and silicon ethoxide in propanol led to both powdered and gel samples [5]. For simplicity, all samples (gels, glasses and crystalline compounds) are represented in terms of their composition Al : Si : Ge as $X(Al_2O_3)$–$Y(SiO_2)$–$Z(GeO_2)$. The water content is not specified.

2.2. X-ray absorption spectroscopy

X-ray absorption spectra were recorded at the French synchrotron radiation facility, LURE, on spectrometers EXAFS1 on DCI (Ge edge, 11104 eV) and the SA72 line on Super ACO (Al and Si edges, 1560 and 1839 eV, respectively). For the first of these, the spectrometer was equipped with a channel cut Si[331] monochromator, and the spectra recorded in transmission mode at 77 K on powdered samples made up as thick mulls in paraffin oil, and mounted between the parafilm windows of stainless steel sample holders. Sampling for silicon edge spectra (InSb[111] monochromator) was performed on microporous nylon (pore size 5, 10 or 20 μm), on which transmission spectra were recorded at room temperature. In the case of aluminium edge spectra (quartz monochromator), the data length is limited by the proximity of the silicon edge also present in all compounds. Powdered samples were dispersed over ~1 cm^2 on double-faced adhesive tape mounted on copper slides and the signal detected as the total electron yield at room temperature. Additional experimental details are available from the authors. All data analysis was performed using the EXAFS and XANES programmes written by Michalowicz [9].

2.3. Macroscopic structural evolution in the Al_2O_3–SiO_2–GeO_2 system

Mullite gel of composition $3Al_2O_3$–$2SiO_2$–$10H_2O$ undergoes transformation to a porous glass (specific surface area ~300–400 $m^2\ g^{-1}$) at ~300°C, and at 600°C its composition is close to $Al_6Si_2O_{10.77}(OH)_{0.46} \cdot H_2O$. At higher tempera-

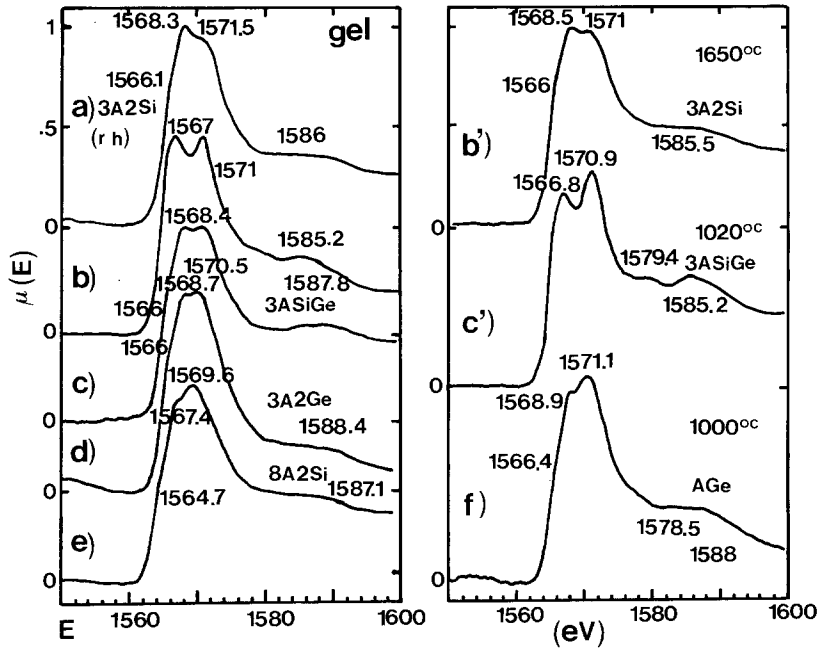

Fig. 1. Near edge spectra (1550–1600 eV) at the aluminium absorption edge of $x(Al_2O_3)$–$y(SiO_2)$–$z(GeO_2)$ phases (rh: rapid hydrolysis).

ture, around 940°C, the porosity decreases sharply as the glass densifies and nucleation of mullite commences, although the glass phase persists to above 1400°C. For the composition Al_2GeO_5, crystallisation starts near 900°C, and is complete below 1300°C and the compound has the mullite structure. The Raman spectrum indicates a more ordered arrangement [5] than that in the mullite having composition $3Al_2O_3$–$2SiO_2$ (or $x = 0.25$, according to Cameron's notation $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$ [10], but differs from that of sillimanite ($x = 0$, Al_2SiO_5), where static disorder in the occupation of tetrahedral sites by Al^{3+} and Si^{4+} no longer exists; it is important to note that this naturally occurring phase is formed under pressure.

3. Results

3.1. Al edge

The normalised near edge spectra, in the energy range 1560–1600 eV (fig. 1) all show two maxima. By comparison with the corresponding spectra of model compounds of known crystal structure, it may be concluded that, in the present case, the aluminium atoms are predominantly hexacoordinate; the XANES of a series of model aluminosilicates all present one maximum when aluminium is tetracoordinate, and two maxima when aluminium is in an octahedral environment [11]. This conclusion is further supported by the presence, to the low energy side of the first maximum, and on the absorption edge itself, of an inflexion point at 1566.0 eV. An edge feature of this type was observed at this energy in materials containing hexacoordinate aluminium, but is notably absent in model compounds containing only tetracoordinate Al. Raman spectroscopic data have also been interpreted in terms of a local structure of the spinel type, both for gels and glasses [5]. The possible presence of a certain proportion of tetracoordinate aluminium cannot, nevertheless, be excluded, near edge spectra of model compounds (illite, muscovite) containing both hexa- and tetracoordinate aluminium [11] differing little from those containing hexacoordinate atoms only.

The relative intensity of the first and second maxima is variable. While this observation is not fully understood, it is interesting to note that in the near edge spectra of the mullite phases, whether gel or crystalline, and prepared by slow or rapid hydrolysis, the first maximum is more intense than the second, that substitution of germanium for silicon in the two gels of composition $3Al_2O_3$–$0.5GeO_2$–$1.5SiO_2$ and $3Al_2O_3$–$2GeO_2$ redresses this inequality, while thermal treatment of the latter leads to an increase in intensity of the second maximum relative to the first.

In aluminosilicates containing hexacoordinate aluminium (corundum, diaspore, gibbsite, pyrophyllite, etc.), the first and second maxima occur at 1567.6–1568.5 and 1570.1–1572.4 eV, respectively [11]. Tetrahedral AlO_4 presents a XANES spectrum of single maximum at lower energies ($\Delta E \approx 2$ eV). Positions of the maxima of the spectra of fig. 1 are in agreement with a hexacoordinate aluminium environment. Slight variations in the positions of the first maximum – a 'chemical shift' – can be related to the 'ionicity' of the Al–O bond, which must, in turn, be related to the nature of the second neighbours – silicon or germanium. In $8Al_2O_3$–$2SiO_2$ and $3Al_2O_3$–$2GeO_2$, the first maxima are observed at 1567.4 eV and 1568.7 eV, respectively, and may imply that compounds having silicon as second neighbours have a first absorption peak at lower energies (bond of more 'ionic character') than those with germanium (Al–O bond of more 'covalent character') in the second coordination sphere. The trend is observed in other members: mullite gel does, indeed, have a 'low energy' first maximum, and other compounds containing germanium (Al_2GeO_5 gel, $3Al_2O_3$–$0.5GeO_2$–$1.5SiO_2$ gel) a 'high energy' maximum. We suggest that in this two compound, the second neighbour is germanium, and not silicon. Conversely, in crystalline $3Al_2O_3$–$0.5GeO_2$–$1.5SiO_2$, the maximum of the first peak is at 1566.8 eV, which may indicate a change in the nature of the second neighbours on thermal treatment.

The form of the second maximum varies from compound to compound, with the appearance of

shoulders at higher energies in certain cases (e.g., crystalline $3Al_2O_3$–$0.5GeO_2$–$1.5SiO_2$). By comparison with aluminosilicates of known structure [11], regular AlO_6 octahedra give rise, in XANES, to a second rather symmetrical peak, whereas the presence of shoulders above the second maximum are associated with a distorted octahedral environment. In the present case, only crystalline $3Al_2O_3$–$0.5GeO_2$–$1.5SiO_2$ shows these features distinctly; Al_2GeO_5 and the mullites represent an intermediate stage (possible site symmetry 3 or m as in corundum or diaspore), whereas the spectra of the remaining gels ($8Al_2O_3$–$2SiO_2$, $3Al_2O_3$–$2GeO_2$ and $3Al_2O_3$–$0.5GeO_2$–$1.5SiO_2$) can be interpreted in terms of regular AlO_6 octahedra.

3.2. Si edge

The near edge spectra (fig. 2(a–c)) of crystalline phases are more structured than those of gels, but the maximum of the absorption edge, and of the shoulder to the high energy side, remain unchanged for all samples. More detailed information can be derived from the Fourier transformed EXAFS spectra of three materials taken as examples: $8Al_2O_3$–$2SiO_2$, $4Al_2O_3$–$6SiO_2$ (both gels) and crystalline $3Al_2O_3$–$2SiO_2$ (fig. 2(d–f)). Not only is the expected evolution between a gel and crystalline phase seen, with backscattering in the former limited to that from a first shell of atoms (oxygen) and extended in the latter through the laying down of long distance order, but also differences in the local structure of gels having different compositions are seen. Thus the silica-rich gel already has some contributions to the EXAFS from longer distance atomic shells, compared with the alumina-rich gel, results which may be rationalised by the glass-forming character of silicon. Inclusion of the (Si–O) phase correction and adjustment of the energy offset until the maxima of the modulus and imaginary parts, and the zero of the real part of the Fourier transform, coincided, allowing determination of the silicon–oxygen distance. For the two gels, the distance is practically identical (0.1655 ± 0.0005 nm) but longer than that in crystalline mullite (0.1615 ± 0.0005 nm). This latter value is in good agreement with that determined by X-ray diffraction in Al_2SiO_5, where both aluminate and silicate tetrahedra are well ordered

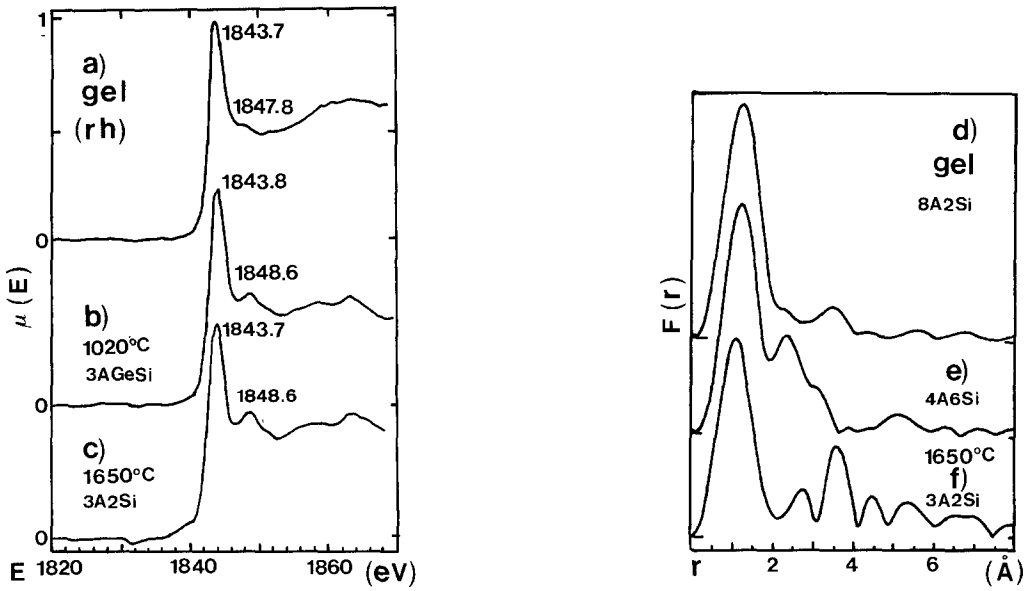

Fig. 2. (a–c) Near edge spectra (1820–1870 eV) at the silicon absorption edge. (d–f) Fourier transformed EXAFS spectra ((a) rh: rapid hydrolysis).

[12]. The contraction on thermal treatment, probably related to the presence of bridging hydroxyl groups in the former, is the structural consequence of the densification which accompanies the transition from the gel to the glass or the crystalline state.

3.3. Ge edge

The Al_2O_3–GeO_2 system is taken as an example to demonstrate the local structural evolution around germanium through the gel, glass and crystal states. Hexagonal and rutile forms of GeO_2 have distinct germanium atom environments, composed of four oxygen atoms at 0.176 nm in the hexagonal form, and a distorted octahedral environment of four oxygen atoms at 0.186 nm and 0.189 nm in the rutile type. In Al_2GeO_5, the EXAFS results (fig. 3) indicate a tetracoordinate arrangement, with a Ge–O bond length of 0.177 nm in the gel, and 0.176 nm in the crystal (thermal treatment at 1300°C). Germanate tetrahedra are thus present from the outset, and the bond length is relatively unaffected by densification effects, as observed previously in gels in the GeO_2–SiO_2 system [13], by contrast with the contraction observed around silicon (see above). Raman spectroscopy has also provided evidence for GeO_4 groups in this system, but only in glasses heated above 1000°C [4,5]. X-ray diffraction, on the other hand, has shown the presence of a certain proportion of germanium atoms in octahedral sites [14], although the present EXAFS data provide little evidence that can be interpreted in these terms. More distant atom shells are also observable in the Fourier transformed EXAFS spectrum (fig. 3), both in the gel and, more distinctly as expected, in the crystalline material. However, the intermediate glass (thermal treatment at 800°C) has no long distance order. A similar phenomenon has been observed to occur around zirconium in NASICON $Na_3Zr_2Si_2PO_{12}$ [15].

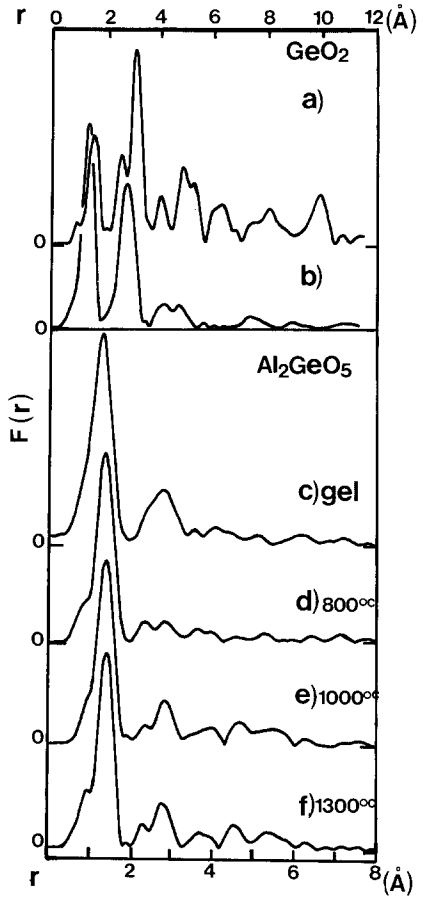

Fig. 3. Germanium absorption edge: Fourier transformed EXAFS spectra of rutile (a) and hexagonal (b) forms of GeO_2 and of Al_2GeO_5 gel (c), glass (d) and crystalline phases (e, f).

4. Conclusion

In conclusion, we have shown that X-ray absorption spectroscopy is of particular value in the study of short range order within the Al_2O_3–SiO_2–GeO_2 system. In the gel, glass and crystalline phases, aluminium is hexacoordinate, silicon and germanium tetracoordinate. The metal–oxygen bond lengths have different sensitivities to macroscopic changes, essentially densification, induced by thermal treatment. Even gels have local structural order beyond the first coordination sphere, but this order is lost in the intermediate glass.

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